ORIGINAL PAPER

QUARTZ CRYSTAL MICROBALANCE USED AS SENSOR FOR PESTICIDES DETECTION

IOANA DANIELA DULAMA[1], CRISTIANA RADULESCU[1,2*], IOAN ALIN BUCURICA[1*], SOFIA TEODORESCU[1], RALUCA MARIA STIRBESCU[1], GHEORGHE VALERICA CIMPOCA[3], DORIN DACIAN LET[1], ION VALENTIN GURGU[1]

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Abstract. *Along the time, the pesticides, on the one hand, represented a solution for covering human needs and combating pests, thus helping peoples lives, and on the other by their continuous use, led to the contamination of food and natural resources with substances dangerous for humans, many of which being carcinogenic. The inadequate use of pesticides may contaminate the soil, water reservoirs, superficial and groundwater, biota and consequently ending up contaminating people. This study highlighted that quartz crystal microbalance (QCM) technique corelated with attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) would be able to detect different pesticides in aqueous solution in order to establish their ilegal used in agriculture under various name.*

Keywords: *Dithane M-45, Fastac, Optimol, QCM, ATR-FTIR.*

1. INTRODUCTION

Usually, pesticides are well-defined organic compounds, natural or synthetized substances, used to prevent or control weeds (i.e. herbicide), fungi and moulds (i.e. fungicide), insects (i.e. insecticide), rodents (i.e. rodenticide) and nematodes (i.e. nematicide). These polluting substances, which can be persistent, active and slowly biodegradable in the environment for a long time after contamination, are used in agriculture to kill pests and protect crops (e.g. plant-growth regulators, defoliants or desiccants). The main classes of pesticides, according to their chemical nature, are [1-3]: organophosphorus pesticides (OPPs), organochlorine pesticides (OCPs), carbamats and pyrethroids. Many environmental problems are caused by use, overuse or misuse of pesticides, particularly with a long damage risk on life quality. Therefore the knowledge and understanding of pesticides used in agriculture is an important step in applying good health and safety standards. The use of pesticides should be optimized, bearing in mind the safety to producers and consumers as well as the environmental impact, by respecting the national and international regulations [1-5]. *In-situ* monitoring and analytical methods [6-16], faster, eco-friendly and low cost-effective, can facilitate the collection of data concerning particular target pesticides that may impact on

**Corresponding authors: Cristiana Radulescu, Ioan Alin Bucurica*
[1] Valahia University of Targoviste, Institute of Multidisciplinary Research for Science and Technology, 130004 Targoviste, Romania. E-mail: bucurica_alin@yahoo.com.
[2] Valahia University of Targoviste, Faculty of Science and Arts, 130004 Targoviste, Romania.
E-mail: radulescucristiana@yahoo.com.
[3] Academy of Romanian Scientists, 050094 Bucharest, Romania. E-mail: valcimpoca@yahoo.com.

human health and the environment. It is almost impossible to clearly elect a technique as being the most suitable for the analysis of pesticides, as this depends on many factors, such as contaminant concentration and characteristics, their chemical structure, degradation type, etc.

In the last years, some ideas [1-4] were given concerning the choice of an appropriate technique to solve environmental contamination with pesticides. However, dangerous pesticides continue to be used in many countries, especially developing countries, and the acreage where serious damage has been inflicted have been increasing all over the world. In this paper were used quartz crystal microbalance (QCM) sensors in order to detect three banned pesticides, but still used illicitly, in aqueous samples.

2. MATERIALS AND METHODS

2.1. MATERIALS

In this investigation the QCM technique was used in order to evaluate sensor response for three pesticide types (Table 1) such as: *Dithane M-45* – non-systemic agricultural fungicide with action by contact (mancozeb that means a combination between two dithiocarbamates, coordination polymers, such as: *maneb* and *zineb*, with chemical formulas $(C_4H_6MnN_2S_4)_n$ and $C_4H_6N_2S_4Zn$, respectively, and structure presented in Figs. 1 and 2), *Fastac* – broad-spectrum insecticide (alpha-cypermethrin a synthetic pyrethroid with chemical formula $C_{22}H_{19}Cl_2NO_3$ and structure shown in Fig. 3) and *Optimol* – molluscocide with action by contact and ingestion (metaldehyde or 2,4,6,8-tetramethyl-1,3,5,7-tetroxocan as active substance, that means a cyclic tetramer of acetaldehyde with formula $C_8H_{16}O_4$ and chemical structure presented in Fig. 4).

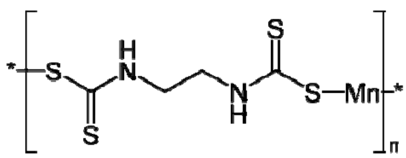


Figure 1. Chemical structure of maneb: Manganese ethylene-1,2-bisdithiocarbamate, polymer (polymeric complex of manganese with the ethylene bis(dithiocarbamate) anionic ligand).

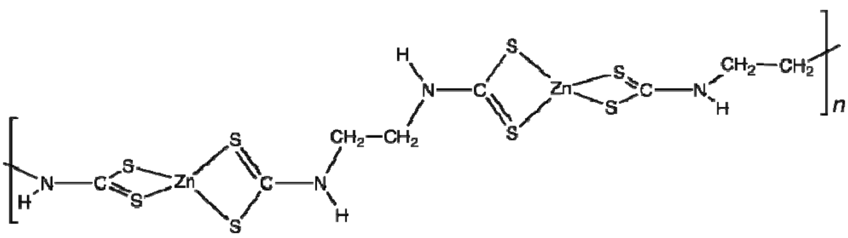


Figure 2. Chemical structure of zineb: zinc ethane-1,2-diylbis(dithiocarbamate), coordination polymer, (Zineb).

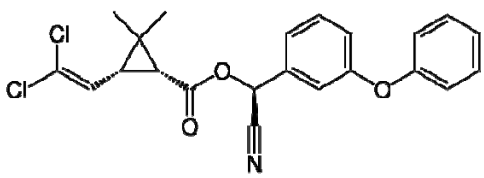


Figure 3. Chemical structure of alpha-cypermethrin: [Cyano-(3-phenoxyphenyl)methyl]3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropane-1-carboxylate.

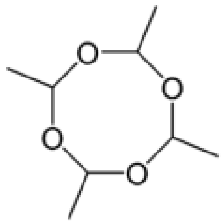


Figure 4. Chemical structure of metaldehyde: 2,4,6,8-tetramethyl-1,3,5,7-tetroxocan.

Table 1. Pesticides description.

Pesticide	Active substance	Molecular formula	IUPAC name	Information*/ Toxicity
Dithane M-45			*Mancozeb* that means a combination between two dithiocarbamates, coordination polymers, such as: *maneb* and *zineb*	Agriculture fungicide with multi-site, protective action on contact (considered as a low risk group but still banned in US).
	Maneb	$(C_4H_6MnN_2S_4)_n$	Manganese ethylene-1,2-bisdithiocarbamate, polymer (polymeric complex of manganese with the ethylene bis(dithiocarbamate) anionic ligand)	
	Zineb	$C_4H_6N_2S_4Zn$	Zinc ethane-1,2-diylbis(dithiocarbamat, coordination polymer	
Fastac	Alpha-cypermethrin	$C_{22}H_{19}Cl_2NO_3$	[Cyano-(3-phenoxyphenyl)methyl]3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropane-1-carboxylate	Broad-spectrum insecticid, which means it kills beneficial insects as well as the targeted insects. Is moderately toxic through skin contact or ingestion. It may cause irritation to the skin and eyes.
Optimol**	Metaldehyde	$C_8H_{16}O_4$	2,4,6,8-tetramethyl-1,3,5,7-tetroxocan	Chemical molluscicides (banned in US and EU).

**Banned status according to the United Nations Treaty (known as the Stockholm Convention on Persistent Organic Pollutants), which has been signed by the majority of countries. One notable exception is the USA, which has its own list of banned substances covering many of the same pesticides.*
*** Plant Protection Products listed in 'Pesticides 2012' that may no longer be marketed or used.*

The sellected pesticides were dissolved and diluted with distilled deionized water (Milli-Q Water System Millipore until the concentration of active substance reach 10.00 mg/L, 0.10 mg/L, 1.00 µg/L and 0.01 µg/L. The obtained solutions were coded as can be seen in Table 2.

Table 2. Active substance content in pesticide solutions.

Concentration of active substance in aqueous solution	Dithane M-45	Fastac	Optimol
10 mg/L	D5	F5	O5
100 μg/L	D7	F7	O7
1 μg/L	D9	F9	O9
0.01 μg/L	D11	F11	O11

2.2. METHODS

The initial samples (before dilution) were analyzed using Fourier transform infrared spectrometer Vertex 8000 (Bruker) equipped with ATR accessory, which adsorbs infrared radiation in the range of 400-8000 cm^{-1}, with good accuracy (0.1% T) and high spectral resolution (0.2 cm^{-1}) [17-19]. ATR-FTIR spectroscopy allows the rapid and reagentless, analysis of liquid and solid samples and was used to investigate the chemical groups of organic compounds contained in pesticide samples. For a good reproducibility, all samples were analysed in triplicate at room temperature (22°C) and the spectra (e.g. Fig. 5) were drawn using average value.

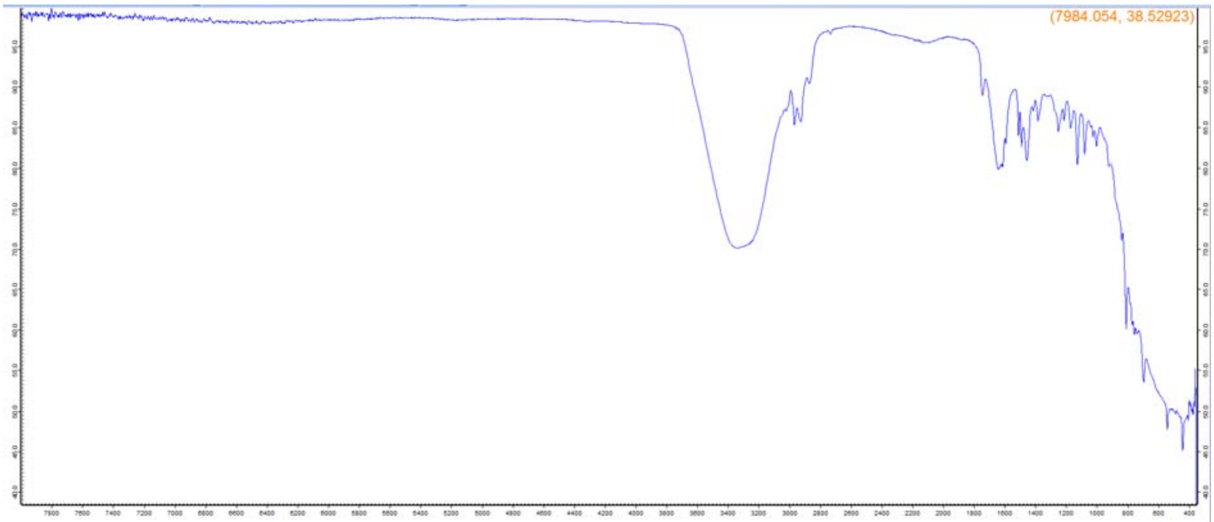


Figure 5. FTIR spectrum of Fastac.

Quartz crystal microbalance QCM200 (Stanford Research Systems) was successfully used in diverse applications such as: the detection of toxic gases (aromatic hydrocarbons, ammonia, SO_2 etc.) [20], toxic substances (cyanide) [21], aflatoxins [22, 23], for thin film deposition [24], to determine viscosity and viscoelasticity [25] etc.

QCM is widely used due to its sensitivity and its ability to determine in real time the variation of the adsorbed mass at the sensor surface, in the field of ng/cm^2. For this study were used chrome-gold electrodes (CrAu) covered with self-assembled monolayers (SAM) in order to increase the limit-of-detection (LOD) up to 18 ng/cm^2 for a frequency shift of 1 Hz. The SAM was obtained using ethanethiol (1%). All diluted samples were analysed in static mode, in triplicate at room temperature, and all results were presented as an average value.

3. RESULTS AND DISCUSSION

Attenuated total reflection–Fourier transform infrared spectroscopy was used in order to identify the groups of pesticide samples. This technique is used for quality control and fingerprinting of various samples, and also, allows a complex characterization of different functional groups [26-31]. In this research, Fourier transform infrared spectrometry was used with succes in investigated pesticides screening and spectral data are presented in Table 3.

Table 3. Infrared spectral data of pesticide samples

Pesticide	Wavenumber [cm^{-1}]	Relative intensity*
Dithane M-45	3279 / 2940 / 1650 / 1275 /1030 /1000 / 850 / 700 /	m / w / w / m / w / w / w / w
Fastac	3305 /1610 / 1600 / 1560 / 1280 / 1250 / 800 / 400	w / m / w / w / w / m / m / m
Optimol	3225 / 1660 / 1280 / 1020 /1000 / 600 / 400	s / s / w / w / w / w / m / w

** s – strong; m – medium; w - weak*

In FTIR data of *Dithane M-45* can be observed few bands: 1650-1550 cm^{-1} for NH amino substituted group (deforming vibrations), 2940 cm^{-1} for NH group, 1300-1000 cm^{-1} to simple stretching vibrations bonds, 850-700 cm^{-1} deforming vibrations of H-N-CS_2-polyatomic systems, 3279 cm^{-1} is assigned to –NH-CH_2-CH_2-NH- ethylenediamine substitute group, 1275-1030 cm^{-1} for C=S.

In the case of *Fastac*, the 1610-1600 cm^{-1} signal is assigned to -COO- group linked to a cyano group (-C≡N), 800 cm^{-1} and 400 cm^{-1} represents the C-Cl bond, the values between 3500 cm^{-1} and 3300 cm^{-1} are for arC-Hst, the medium intensity band from 1250 cm^{-1} are assigned to arC-H bond.

The infrared spectral data of *Optimol* presents a strong signal (1660 cm^{-1}) assigned to CH_3 group, linked as H_3C-C-O-. This signal is correlated with the strong one (3300 - 3200 cm^{-1}), representing the octocycle CH group. The peaks from 600 cm^{-1} and 400 cm^{-1} were assigned to -C-O-C group, as well.

All pesticide samples (Table 2) were investigated using CrAu sensors covered with ethanethiol self-assembled-monolayer, in static mode: 0.5 mL sample place directly to sensor, for about 30 minutes. However, after 150 seconds the frequency shift tends to zero. The obtained data were used to calculate the sensor response (frequency shift in time [Hz/s]) and to draw the linear or polynomial regression. For Dithane M-45 was observed linear regression for all samples (i.e. D5, D7, D9, D11) with R^2 determination coefficient values in the range of 0.8945–0.9693 (Fig. 6). For Fastac and Optimol the fitting curves show polynomial regression for all samples (i.e. F5, F7, F9, F11 and O5, O7, O9, O11) with R^2 determination coefficient values in the range of 0.9882–0.9946 for insecticide samples (Fig. 7), respectively 0.9826–0.9963 for moluscocide samples (Fig. 8).

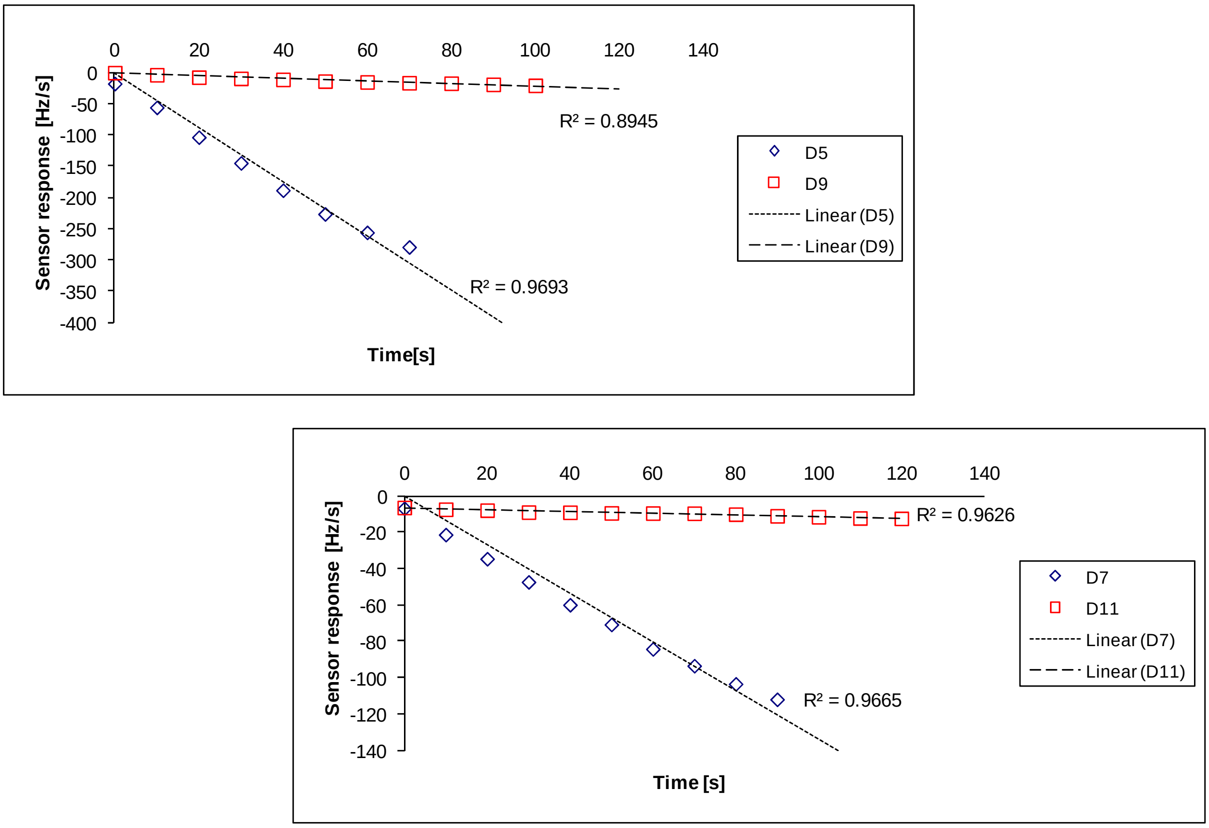


Figure 6. QCM sensor response for all fungicide samples (i.e. *Dithane M-45*).

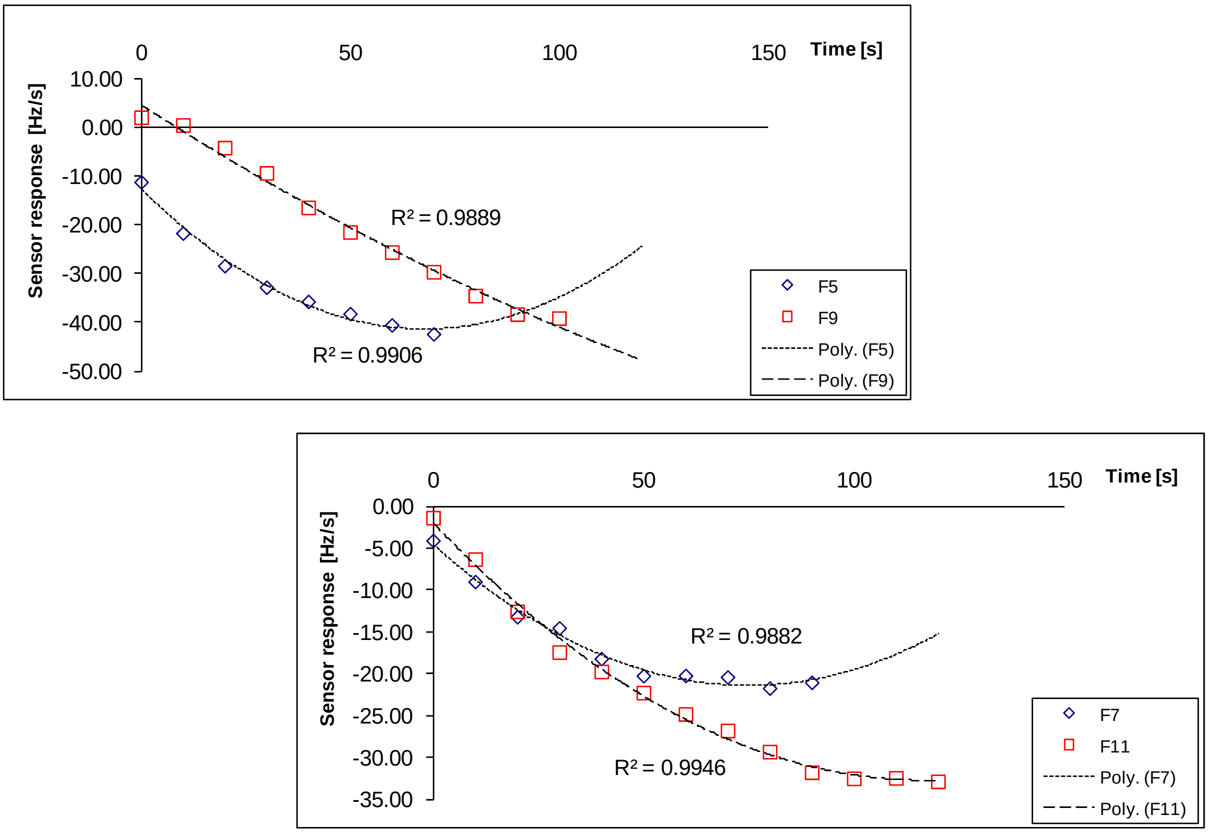
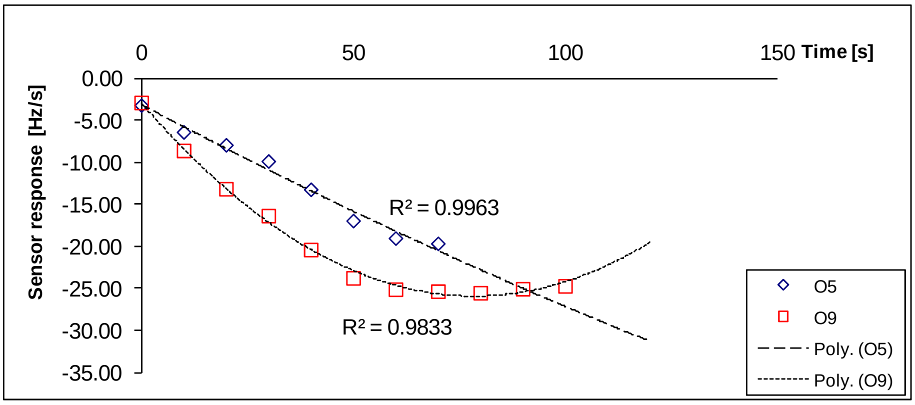


Figure 7. QCM sensor response for all insecticide samples (i.e. *Fastac*).



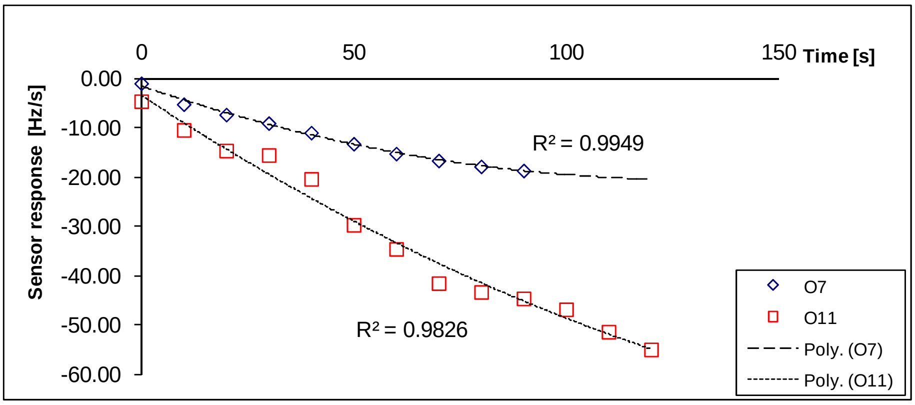


Figure 8. QCM sensor response for moluscocide samples (i.e. *Optimol*).

Considering the fact that the adsorbed mass on QCM sensor surface is inversely proportional to sensor response, it can be observed that for fungicide *Dithane M-45* with active substance concentration of 0.01 µg/L the recorded signal is very poor and probably is under the limit of detection. For the other two pesticides (*Fastac* and *Optimol*) the recorded signal was good even for the lowest concentration of active substances.

4. CONCLUSION

The pesticides that were selected for this study (i.e. *Dithane M-45*, *Fastac*, and *Optimol*) are banned, as they are classified as persistent organic pollutants (POPs). The proposed solution for the determination of pesticides using quartz crystal microbalance techniques is advantageous in terms of the time required for sample preparation, and the time devoted to actual analysis. The fact that microbalance provides real-time results allow its use in various fields. The used sensor show high sensitivities at low concentration values (10 ng/L) and is considered a promising method for the direct analysis of aqueous samples. The obtained data establish the potential for QCM sensor for the use in pesticide analysis at alarm levels.

REFERENCES

[1] ***** Directive 91/414/EEC – *Evaluation, authorisation, approval of active substances at EU-level and national authorisations of PPPs*, 1991.

[2] Hardy, A., Fontier, H., *European Food Safety Authority Journal*, **9**(6), e961, 2011.
[3] Nienstedt, K.M. et al., *Science of the Total Environment*, **415**, 31, 2012.
[4] Brown, C.D., van Beinum, W., *Environmental Pollution*, **157**, 3314, 2009.
[5] ***** Codex alimentarius - *Maximum Residue Limits for Pesticides*, 2009. Available online in http://www.codexalimentarius.net.
[6] Luo, X. et al., *Electroanalysis*, **18**(4), 319, 2006.
[7] Manisankar, P. et al., *Talanta*, **68**(3), 686, 2006.
[8] Manisankar, P. et al., *International Journal of Environmental Analytical Chemistry*, **89**(4), 245, 2009.
[9] Panasyuk-Delaney, T. et al., *Analytica Chimica Acta*, **435**(1), 157, 2001.
[10] Pellicer, C. et al., *Analytical Methods*, **2**(9), 1280, 2010.
[11] Sun, X. et al., *Sensor Letters*, **8**(2), 247, 2010.
[12] Shapovalova, E.N. et al., *Journal of Analytical Chemistry*, **64**, 164, 2009.
[13] Paiga, P. et al., *Analytical Letters*, **42**, 265, 2009.
[14] Niessen, W.M.A., *Journal of Chromatography A*, **1217**, 4061, 2010.
[15] Boti, V.I. et al., *Journal of Chromatography A*, **1146**, 139, 2007.
[16] Boti, V.I. et al., *Journal of Chromatography A*, **1146**, 148, 2007.
[17] Bintintan, A. et al., *Revista de Chimie*, **68**(4), 847, 2017 .
[18] Buruleanu, L.C. et al., *Analytical Letters*, **51**(7), 1039, 2018.
[19] Teodorescu, S. et al., *Revista de Chimie*, **68**(4), 869, 2017.
[20] Ogimoto, Y. et al., *Sensors and Actuators B: Chemical*, **215**, 428, 2015.
[21] Dulama, I.D. et al., Quartz Crystal Microbalance: Nano-Sensor For Cyanide Detection, *Journal of Science and Arts*, **2**(19), 201, 2012.
[22] Dulama, I.D. et al., Detection of aflatoxin using Quartz Crystal Microbalance, *Journal of Science and Arts*, **2**(13), 341, 2010.
[23] Teresa, M. et al., *Sensors and Actuators B: Chemical*, **48**(1-3), 383, 1998.
[24] Cimpoca, G.V. et al., Self assembled monolayer of ethanthiol on gold surfaces by quartz crystal microbalance, *CAS: 2009 International Semiconductor Conference*, **Vols. 1 and 2**, 135, 2009.
[25] Dulama, I.D. et al., Analysis of liquids and viscoelestic films by quartz crystal microbalance, *2010 International Semiconductor Conference (CAS)*, **Vols. 1 and 2**, 225, 2010.
[26] Radulescu, C., *Revista de Chimie*, **56**(2), 151, 2005.
[27] Radulescu, C, Tarabasanu-Mihaila, C., *Revista de Chimie*, **55**(2), 102, 2004.
[28] Radulescu, C, Tarabasanu-Mihaila, C., Hossu, A.M., Ionita, I., *Revista de Chimie*, **55**(12), 1006, 2004.
[29] Radulescu, C, Hossu, A.M., *Revista de Chimie*, **56**(7), 742, 2005.
[30] Radulescu, C, Tarabasanu-Mihaila, C., Hossu, A.M., Ionita, I., *Revista de Chimie*, **55**(11), 889, 2004.
[31] Pretsch, E., Buhlmann, P., Badertscher, M., *Structure determination of organic compounds. Tables of spectral data*, 4th Edition, Springer, 2009.